

THE SIGNIFICANCE OF BROMIDE ON THE DRINKING WATER QUALITY OF SACRAMENTO-SAN JOAQUIN DELTA WATERS

Introduction

Waters of the Sacramento-San Joaquin Delta serve nearly 22 million people living in the Bay-Delta region and southern California. The Delta as a drinking water supply is, therefore, important to the public health and economy of the State.

Municipalities taking water from the Delta are currently faced with an array of challenges. Besides having to compete for increasingly scarce water supplies, new State and federal drinking water regulations are requiring increasing levels of treatment. The cost of treating Delta waters to meet the new standards will be staggering to the drinking water industry.

Disinfection, which is critical to protect against microbial disease, produces chemical byproducts that may pose other health risks such as cancer. Trihalomethanes (THMs) are some of the types of disinfection byproducts (DBPs) that can be formed when chlorine and chloramines are used as disinfectants. Chlorine and chloramines have been the preferred disinfectants of choice because of lower costs and high effectiveness in controlling bacterial growth in the water distribution system.

THMs consist of four chemical compounds: chloroform, dibromochloromethane, bromodichloromethane, and bromoform. Currently, THMs are the only regulated DBPs. The current maximum contaminant level (MCL) for total THMs is 0.100 mg/L. However, new U.S. Environmental Protection Agency regulations, which will take effect in November 1998 and referred to as the Disinfectants-Disinfection Byproducts (D-DBP) Rule, will lower MCLs for total THMs and set new MCLs for other DBPs including bromate and the sum total concentration of five specified haloacetic acids (HAA5).¹ The new regulations will also require water utilities to utilize specified best available technologies (BATs) for meeting the MCLs.

To meet the MCLs for THMs and HAA5, BATs to be utilized for reducing DBP precursor concentrations prior to disinfection with chlorine or chloramines include enhanced coagulation and granular activated carbon adsorption. To meet the bromate MCL, the BAT will consist of controls on variables which affect bromate formation during ozonation, such as bromide concentrations, total organic carbon concentrations, pH, ammonia, alkalinity, hydrogen peroxide levels, temperature, and contact time.

The new MCLs under the D-DBP Rule will be set in two stages. It is anticipated that the D-DBP Rule will be implemented according to the following table:²

Current MCLs and Proposed MCLs Under the D-DBP Rule (mg/L)

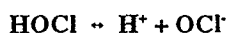
Disinfection Byproduct	Current MCLs	Stage 1 MCLs (November 1998)	Stage 2 MCLs (May 2002)
Total THMs	0.100	0.080	0.040
HAA5	None	0.060	0.030
Bromate	None	0.010	0.005

It is important to note that the proposed MCLs are not based on human health criteria. The proposed Stage 1 MCLs are based on technical and economic feasibility of achieving the MCLs with the specified BATs. The proposed Stage 2 MCLs are currently placeholders set at one-half the MCLs under Stage 1. The final Stage 2 MCLs will be determined based on further research on the health effects of DBPs and treatment technologies for reducing DBP formation.

Disinfection Byproducts - Chemistry

Chlorination

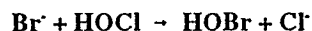
Free chlorination is the predominant method of disinfection in water treatment practice. THMs are one group of DBPs formed when soluble organic compounds are oxidized by free chlorine. During disinfection, molecular chlorine reacts with water by the following reversible reactions:



The relative amounts of hypochlorous acid (HOCl) and hypochlorite (OCl⁻) produced in the above reactions are a function of pH. These chlorine species, known as free chlorine, are the disinfection agents in the chlorination process. Free chlorine (HOCl and OCl⁻) also reacts with soluble organic compounds to form THMs by the following general reaction:



If bromide is present in the water, it competes with free chlorine to form brominated THMs (dibromochloromethane, bromodichloromethane, and bromoform). The bromide is oxidized to hypobromous acid (HOBr) according to the following reaction:



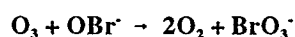
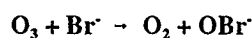
Hypobromous acid then competes with free chlorine (particularly hypochlorous acid) to produce THMs by the following general reaction:



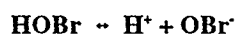
Because the atomic weight of bromine [79.91] is heavier than that of chlorine [35.45], the molecular weight of brominated THMs increase in proportion to the number of bromine atoms present in the THM compound: CHCl_3 [119.36], CHCl_2Br [163.82], CHClBr_2 [208.82], and CHBr_3 [252.74]. As a result, bromide will increase the concentration of total THMs that is formed. This could result in more frequent exceedances of the MCLs.

Ozonation

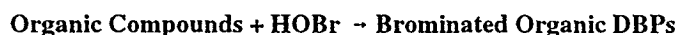
Ozonation is increasingly being used for disinfection of drinking water supplies. In the presence of bromide, oxidation by ozone will lead to the formation of hypobromite (OBr^-). Further oxidation of hypobromite leads to the formation of bromate (BrO_3^-):



The amount of hypobromite available for oxidation to bromate is dependent on pH, based on the relative amounts of hypobromous acid and hypobromite:



In addition, hypobromous acid may react with organic compounds to form brominated organic DBPs (e.g., bromoform, dibromoacetic acid, and monobromoacetic acid):



An increase in pH will result in an increase in bromate formation. Bromate formation will also be increased when bromide concentrations in the water supply are increased.

DBP Precursors - Removal Requirements

Bromide and organic matter are the major precursors that must be controlled. Stage 1 of the D-DBP Rule will require reducing the total organic carbon (TOC) concentration in water supplies prior to adding disinfectant. TOC removal will be based on the source water alkalinity. A specified percentage of the TOC in the source water will need to be removed prior to adding disinfectant:

Proposed TOC Removal Requirements Under the D-DBP Rule³

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L)		
	0 - 60	> 60 - 120	> 120
≥ 2 - 4	35%	25%	15%
> 4 - 8	45%	35%	25%
> 8	50%	40%	30%

While enhanced coagulation or granular activated carbon adsorption will be required to reduce total organic carbon levels in source waters, these treatment technologies are not effective in lowering bromide levels. The most effective way to prevent the formation of brominated DBPs is to reduce the presence of bromide in the source water. As a result, the new drinking water standards under the D-DBP Rule will place a greater need on providing water from sources with low bromide levels.

Human Health Impacts of DBPs

The primary human health concern for THMs and bromate has been the potential carcinogenicity to humans of the chemical compounds. Several animal studies have documented the carcinogenicity of chloroform, bromodichloromethane, bromoform, and bromate. The EPA and the IARC classification of bromoform as a human carcinogen are inconsistent in that EPA classifies bromoform as a probable human carcinogen, while IARC classifies bromoform as not classifiable as a human carcinogen. The carcinogenicity of dibromochloromethane has not yet been well established. EPA classifies dibromochloromethane as only a possible human carcinogen, and IARC classifies bromoform as not classifiable as a human carcinogen. In establishing a maximum contaminant level goal for dibromochloromethane, EPA accounted for the possible carcinogenicity to humans by incorporating an additional safety factor of 10 to the reference dose (RfD) for dibromochloromethane. The RfD was derived from liver toxicity data in subchronic studies in rats. The following table summarizes the current information on the carcinogenicity of DBPs:

Carcinogenicity of DBPs

Disinfection Byproduct	Carcinogenic Potency Factor (mg/kg/day) ⁽¹⁾	Maximum Contaminant Level Goal (µg/L)	EPA Carcinogen Classification	IARC Carcinogen Classification	Theoretical Excess Cancer Risk Level (µg/L) (1)		
					1 X 10 ⁻⁴	1 X 10 ⁻³	1 X 10 ⁻²
CHCl ₃	6.1 X 10 ⁻³ (kidney tumors in male rats)	0	Group B2 (Probable Human Carcinogen)	Group 2B (Possibly Carcinogenic to Humans)	6	60	600
CHCl ₂ Br	6.2 X 10 ⁻² (kidney tumors in male rats)	0	Group B2 (Probable Human Carcinogen)	Group 2B (Possibly Carcinogenic to Humans)	0.6	6	60
CHClBr ₂	RfD (2)	60	Group C (Possible Human Carcinogen)	Group 3 (Not Classifiable as to its Carcinogenicity to Humans)	-	-	-
CHBr ₃	7.9 X 10 ⁻³ (neoplastic lesions in large intestines of female rats)	0	Group B2 (Probable Human Carcinogen)	Group 3 (Not Classifiable as to its Carcinogenicity to Humans)	4	40	400
BrO ₃ ⁻	~ 7 X 10 ⁻¹ (3) (renal tumors in rats)	0	Group B2 (Probable Human Carcinogen)	Group 2B (Possibly Carcinogenic to Humans)	0.05	0.5	5

(1) Assumes average human body weight of 70 kg and daily consumption of 2 liters of drinking water.

(2) Based on RfD of 0.02 mg/kg/day (liver toxicity, subchronic, rats) plus an additional safety factor of 10 for possible carcinogenicity and a relative source contribution of 80%.

(3) Estimated from Theoretical Excess Cancer Risk Level. No Carcinogenic Potency Factor published in IRIS.

Of the THM compounds, bromodichloromethane is the most potent as a carcinogen. The carcinogenic potency of bromodichloromethane is approximately ten times that for chloroform and bromoform. Furthermore, the carcinogenic potency of bromate is approximately ten times that of bromodichloromethane.

In addition to the animal toxicity studies, numerous epidemiology studies have been conducted to determine if there were any associations between chlorination or chloramination of drinking water with the risk of cancer and adverse reproductive effects in humans. Since the 1974 discovery of THMs (which included chloroform, a known animal carcinogen at that time) being formed as byproducts when surface waters were disinfected with chlorine, several studies were conducted to find an association between chlorinated drinking water and cancer mortality. The results of these studies have suggested associations with a wide range of cancer sites, including gall bladder, esophagus, kidney, breast, liver, pancreas, prostate, stomach, bladder, colon, and rectum. The most suggestive associations were with bladder cancer. However, interpretation of these studies were hampered by a lack of control for confounding variables (e.g., age, sex, individual health, smoking history, and other exposures).

Several epidemiology studies were conducted to determine associations between various water quality components of drinking water (including THM levels) and various reproductive or developmental endpoints.

One study conducted in Iowa in 1992 compared water supplies containing relatively high levels of chloroform and other THMs with low birthweight, prematurity, and intrauterine growth retardation. The results of this study suggested an increased risk for intrauterine growth retardation in communities where chloroform levels exceeded 0.010 mg/L. Prematurity was not associated with chloroform exposure, and the risk for low birthweight was only slightly increased. The authors considered the results of this study to be preliminary. Accordingly, the results should be interpreted with caution.

Another study was conducted in Massachusetts in 1993 to determine the relationship between community drinking water quality and a wide range of adverse pregnancy outcomes, including congenital anomalies, stillbirths, and neonatal deaths. A higher frequency of stillbirths was correlated with chlorination and detectable lead levels; cardiovascular defects were associated with lead levels; central nervous system (CNS) defects were associated with potassium levels; and face, ear, and neck anomalies were associated with silver levels. The authors indicated that the findings of this study must be considered as preliminary because of the problems and limitations of the exposure assessment.

The New Jersey Department of Health conducted a cross-sectional study and a case-control study in 1992 to evaluate the association of drinking water contaminants with birth weight and selected birth defects. The cross-sectional study base included 81,055 live births and 599 single fetal deaths between January 1985 and December 1988. The case-control study included interviews with 593 mothers. The results of the studies showed significant elevations in the odds ratio (or relative risk) for several adverse reproductive outcomes:

New Jersey Department of Health Studies (1992) - Odds Ratios

Adverse Reproductive Outcome	Epidemiology Study Type	THM Levels (mg/L)	Odds Ratio (Relative Risk)
Low term birth weight	Cross-Sectional	> 0.080	1.34
Birth defects (overall)	Cross-Sectional	> 0.080	1.53
CNS defects	Cross-Sectional	> 0.080	2.6
Neural tube defects	Cross-Sectional	> 0.080	2.98
Cardiac defects	Cross-Sectional	> 0.080	1.44
Neural tube defects	Case-Control	> 0.080	4.25
Cardiac defects	Case-Control	> 0.015	2.0

The authors of this study indicated that the findings should be interpreted with caution because of possible exposure misclassification, unmeasured confounding, and associations which could be due to chance occurrences.

Most recently, the California Department of Health Services completed an epidemiology study investigating the relationship between THMs in drinking water and spontaneous abortion. This study was published in the March 1998 edition of *Epidemiology*.⁴ In addition, news articles highlighting this study also appeared in the press. The results of this study suggest that pregnant women who drank five or more glasses per day of cold tap water containing ≥ 0.075 mg/L of total THMs were at higher risk of spontaneous abortion. Furthermore, of the four THM compounds, only bromodichloromethane at levels of ≥ 0.018 mg/L was found to be associated with spontaneous abortion. The results of this study may add further weight to the toxicological properties of bromodichloromethane as the primary THM compound of concern. Representatives of DHS recently presented a summary of this study at a recent meeting of the CALFED Water Quality Technical Group. The authors of the study pointed out that no cause-effect relationship could be established with epidemiology studies, and stated that the study needed to be repeated elsewhere in the country to add validation to its findings.

The approach to establishing lower MCLs for total THMs has been based on theoretical excess cancer risk levels to the general population. Because carcinogenicity is considered a toxicological endpoint from chronic use, compliance with the MCLs has been based on the running annual average of quarterly total THM measurements. However, EPA is considering establishing MCLs for the individual THM compounds, with consideration for toxicological effects other than carcinogenicity, including developmental and reproductive toxicity. Consideration of these "more acute" noncarcinogenic effects will require compliance with the new MCLs to be on a more "real-time" basis. The DHS study may serve to strengthen EPA's push in this direction, especially since the study suggests that an increased risk for spontaneous abortion to pregnant women already exists at total THM levels below the currently proposed lower MCL of Stage 1 of the D-DBP Rule.

Bromide in the Sacramento-San Joaquin Delta

The study of DBP precursors and their sources is important for determining how DBP formation might be controlled. The two major precursors are organic matter and bromide. In the southern Delta, where water is diverted by the State Water Project, Central Valley project, and Contra Costa Water District, concentrations of organic matter and bromide are higher than in the waters of the northern Delta.

The Delta has three major sources of bromide. One major source is sea water that enters the western Delta from tidal excursions and mixes with Sacramento river water flowing through the Delta to the export facilities in the southern Delta. The bromide in the water at Clifton Court Forebay and at the Contra Costa Water District intake are attributed to sea water intrusion. Another source of bromide is the San Joaquin River. The primary source of bromide in the San Joaquin River is probably from agricultural return water which contains bromide and is exported from the Delta. Another source of bromide is connate water beneath some Delta islands (e.g., Empire Tract).⁵

Overall, the primary source of bromide in Delta waters is a result of sea water intrusion.⁶ The Department of Water Resources and Metropolitan Water District of Southern California have conducted studies to evaluate sea water intrusion in the Delta.

Because of the stoichiometric relationship between Cl^- and Br^- in sea water, Br^- levels can be predicted based on measured Cl^- levels (provided that no other confounding sources of Br^- and Cl^- are present). The concentration of Cl^- and Br^- in sea water is 18,980 and 65 mg/L, respectively. If Br^- and Cl^- in Delta water were only from sea water diluted with unsalty fresh water, then the following equation could be used to predict Br^- levels, given a measured Cl^- level:

$$\text{Br}^- = 0.00342 \times \text{Cl}^-$$

MWD empirically developed a Br^- to Cl^- relationship in State Water Project water, based on data collected from 1987 through 1989:

$$\text{Br}^- = 0.00289 \times \text{Cl}^- + 0.00671$$

These limited data suggested that most of the Cl^- and Br^- present in Delta water could be explained by sea water intrusion.

In 1990 - 1991, DWR and MWD conducted a bromide intrusion study to evaluate the effect of the ongoing drought on increased salinity in the Delta. Using linear regression, the following relationship was obtained:

$$\text{Br}^- = 0.00327 \times \text{Cl}^- + 0.00496$$

This equation, which falls between the pure sea water relationship and the relationship derived by MWD for SWP water, confirms that sea water is by far the major source of salinity in the Delta.

Based on a nationwide survey conducted in 1991-93 by Gary L. Amy of the University of Colorado, bromide levels in waters of the Delta are typically in the 90th to 95th percentile of levels found nationwide.^{6,7} This means that 90 to 95 percent of the nation's drinking water sources have bromide levels lower than levels typically found in the Delta.

The high levels of bromide found in Delta waters have both economic and public health significance in relation to the new U.S. EPA drinking water regulations soon to be in effect. The BATs required under the D-DBP Rule were established by EPA based on the ability of 90 percent of the nation's water treatment systems to meet the lower MCLs using the BATs. Water treatment systems with current sources of poorer water quality and which can not meet the MCLs may need to utilize more expensive treatment technologies or provide drinking water from sources with lower levels of bromide.

Sacramento River water above the Delta typically contains 1-2 mg/L of total organic carbon and ≤ 0.02 mg/L of bromide. However, water pumped from the Delta to southern California typically contains 3-7 mg/L of TOC and 0.1-0.5 mg/L of bromide. This degradation in water quality, which results in increases in TOC and bromide, presents users of Delta water with tremendous challenges in meeting the new drinking water standards and regulatory requirements.

DBP Formation of Sacramento-San Joaquin Delta Water

To evaluate the effect of TOC and bromide on the formation of DBPs in Delta waters, Stuart Krasner of MWD performed simulation distribution system (SDS) tests for THMs on 25 different combinations of TOC and Br⁻ (a five-by-five matrix) using agricultural drainage from Empire Tract diluted with water from Greenes Landing, with appropriate Br⁻ spikes.⁶ To ensure that these "synthetic" samples could be used to represent differing water qualities of Delta water, a preliminary test was conducted to compare a sample from H.O. Banks with a "synthetic" sample consisting of 90% Greenes Landing water and 10% agricultural drainage, with an appropriate Br⁻ spike. The "synthetic" sample matched the H.O. Banks sample in TOC, UVA, and Br⁻ levels, and similar amounts of individual and total THMs were produced:

Parameter	H.O. Banks Sample	"Synthetic" Sample
TOC (mg/L)	3.65	3.53
UVA (cm ⁻¹)	0.122	0.126
Br ⁻ (mg/L)	0.48	0.48
3-hour SDS THM (mg/L)		
Chloroform	0.012	0.013
Bromodichloromethane	0.034	0.036
Dibromochloromethane	0.067	0.070
Bromoform	0.037	0.038
Total THMs	0.150	0.157
24-hour SDS THM (mg/L)		
Chloroform	0.034	0.034
Bromodichloromethane	0.065	0.073
Dibromochloromethane	0.102	0.117
Bromoform	0.036	0.040
Total THMs	0.237	0.263

Because Greenes Landing and H.O. Banks represent two extremes, the five-by-five matrix of "synthetic" samples was used to address all possible combinations of TOC and Br⁻ that might

be experienced with alternative Delta transfer facilities. The conditions of the SDS tests included an incubation temperature of 25°C, a pH of 8.2, a target chlorine residual of 0.5 - 1.5 mg/L, and an incubation time of 3 hours. The 3-hour incubation time was used to represent a 3-hour prechlorination scenario. If postchloramination is used, Delta water could meet the Stage 1 MCL of 0.080 mg/L for total THMs with up to 4 mg/L TOC, if Br⁻ were not present. As Br⁻ increases, however, the range of TOC levels that would enable compliance with the 0.080 mg/L standard for total THMs shrinks, even with enhanced coagulation (which removes TOC, but not Br⁻). The results indicate that both TOC and Br⁻ in Delta water must be controlled to meet the lower MCL for total THMs:

SDS THM Results (Five-By-Five Matrix) - mg/L

Bromide (mg/L)	Total Organic Carbon (mg/L)				
	1.10	1.36	1.98	3.25	4.15
≤ 0.01	0.024	0.031	0.038	0.064	0.078
0.1	0.043	0.051	0.060	0.080	0.091
0.2	0.060	0.075	0.083	0.103	0.113
0.4	0.075	0.113	0.128	0.142	0.159
0.8	0.088	0.137	0.182	0.241	0.243

Ozonation of Delta waters, followed by chloramination, presents another option for compliance with standards for total THMs. To evaluate the effect of TOC and Br⁻ on the formation of bromate resulting from ozonation of Delta waters, a simulation test for ozonation using a similar five-by-five matrix was conducted. The conditions of the ozone simulation tests included ambient pH of approximately 8, temperature of 20°C, and a target ozone residual of 0.35 ± 0.05 mg/L. To achieve the target ozone residual, an ozone-to-TOC ratio of approximately 2mg/mg was utilized. Under these conditions, the results indicated that Delta water with 2 mg/L TOC and 0.1 mg/L Br⁻ may be capable of achieving the Stage 1 bromate MCL of 10µg/L, whereas an increase in either TOC or Br⁻ may yield a bromate level exceeding the MCL:

Bromate Formation Results (Five-By-Five Matrix) - µg/L

Bromide (mg/L)	Total Organic Carbon (mg/L)				
	1.2	1.6	2.2	2.9	3.7
≤ 0.01	<3	<3	4	<3	7
0.1	6	7	11	12	19
0.2	11	12	19	25	27
0.4 - 0.5	25	23	36	39	49
0.7 - 0.9	29	40	53	57	65

Finally, in December 1996, the California Urban Water Agencies (CUWA) released a draft report entitled Bay Delta Drinking Water Quality Criteria.⁸ This draft report was developed by an expert panel consisting of three water quality and treatment specialists who have specific expertise in the formation of DBPs. The draft report concluded that for currently available advanced water treatment technology to be able to meet probable future drinking water quality standards with water diverted from the Delta, the source water quality should have concentrations less than 3.0 mg/L for TOC and less than 0.05 mg/L for bromide. It was the opinion of the expert panel that these concentrations would be necessary to allow users the flexibility to incorporate either of the technologies evaluated to meet the currently proposed Stage 2 MCLs of the D-DBP Rule. The two technologies evaluated were:

- 1) the use of 40mg/L of alum at a pH of 7.0 and possibly as low as 6.5 in the coagulation process, followed by chlorine disinfection with a chloramine residual in the distribution system; and
- 2) the use of ozone at specific ozone:TOC ratios followed by a chloramine residual.

The chlorine and ozone disinfection criteria were proposed to meet potential 1 or 2 log *Giardia* inactivation requirements. Only the ozone disinfection strategy was considered to provide potential 1 log *Cryptosporidium* inactivation. The TOC value of < 3.0 mg/L is constrained by the formation of total THMs when using enhanced coagulation for TOC removal and free chlorine to inactivate *Giardia*. The bromide value of < 0.05 mg/L is constrained by the formation of bromate when using ozone to inactivate *Cryptosporidium*.

Conclusion

New information on the human health impacts and toxicological properties of brominated DBPs will have a significant impact on the development of new drinking water standards under the D-DBP Rule. The final Stage 2 MCLs under the D-DBP Rule will be determined based on further research on the health effects of DBPs and treatment technologies for reducing DBP formation. BATs which will be required to reduce DBP precursors in source waters are not effective in lowering bromide levels. As a result, the new drinking water standards will place a greater need on providing water from sources with low bromide levels.

References

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